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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Molecular dynamics and linear response computations coupled to picosecond measurements of transient vibrational spectra can in principle reveal atomic trajectories during chemical reactions in solution.

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MOLECULAR DYNAMICS AND
PICOSECOND VIBRATIONAL SPECTRA

by

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The accessible time range for picosecond experimental measurements is now
short enough, and that for molecular dynamics theoretical computation is
now long enough, to significantly overlap. This overlap of theory and
experiment can, at least in principle, be exploited to discover the trajec-
tories of atoms during chemical processes in solution, for example rota-
tional and vibrational relaxation [1], rotational and vibrational dephasing
[2], and chemical reactions. This is significant in that our understanding
of the microscopic basis of processes in liquids has fallen far behind our
understanding of the gas phase. In fact, the atomic motions which form the
microscopic mechanisms for solution processes are hardly understood at all,
even though most processes of interest to most chemists occur in solution.

If we are efficiently to discover these microscopic atomic trajectories,
i.e. the molecular dynamics of solution processes, we must be able to both
theoretically compute and experimentally measure a macroscopic phenomena
which depends closely upon the microscopic trajectories. We believe that
transient vibrational spectra can serve this function. In this paper we
will briefly discuss some of the theory for computing infrared and Raman
spectra from molecular dynamics and will present an example of such a spec-
trum.

Two problems must be solved to compute such spectra. First, a theoreti-
cal approach must be developed which can be applied to the large number of
atoms (~100-1000 including solvent molecules) involved in solution
processes. This gives an incentive to develop ways to compute quantum
reality largely from classical mechanics. Second, a computational approach
must be developed capable of actually calculating spectra in a reasonable
time. The latter problem is a significant one, as to compute 10^{-12} seconds
of real time we find we may need to carry out 10^{12} floating point arith-
metic operations, in order to sufficiently sample phase space.

To compute ir and Raman spectra we need three input functions. From
$V(\{r_i\})$, the potential energy as a function of atomic positions, plus the
initial positions $\{r_i(0)\}$ and velocities $\{\dot{r}_i(0)\}$ of the atoms, we compute,
using classical mechanics, the set of atomic trajectories $\{r_i(t)\}$. From
these trajectories and $\mu(\{r_i\})$, the dipole moment as a function of atomic
positions, we compute $\mu(t)$, the dipole moment of the sample as a function
of time. Using linear response theory [3-6], and suitable quantum correc-
tions [6], we compute an ir spectrum. Finally, we average many such

spectra over runs with different initial $\{r_i(0)\}$ and $\{\dot{r}_i(0)\}$ chosen from the ensemble which represents the experimental conditions of interest, usually a given temperature and pressure. In a similar manner, we use $\bar{\alpha}(\{r_i\})$, the polarizability matrix as a function of atomic positions, to compute the Raman spectrum. While the computations are mathematically relatively straightforward, the number of arithmetic operations is very large and we therefore carry them out on an array processor [7,8].

We have been refining this technique by comparing the computed spectra against known ir and Raman spectra of ordinary gas and liquid samples, i.e. time independent, equilibrium spectra. The results are encouraging. Fig.1 shows an example.
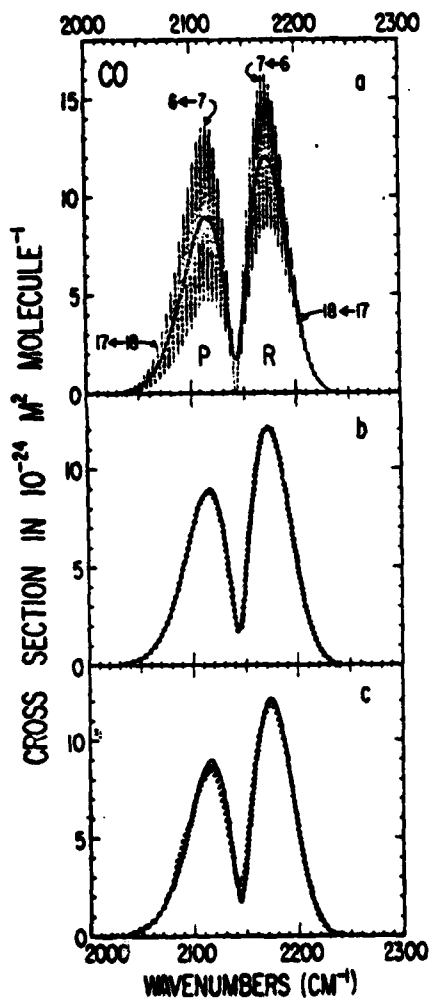

Fig.1 The CO gas phase fundamental vibrational-rotational band at 298 K. The top panel shows the spectrum as computed from summing up all the applicable transitions calculated in the usual way from time dependent quantum perturbation theory. The dashed line shows the rotational transitions making up the P ($\Delta J=-1$) and R ($\Delta J=+1$) branches. The solid line shows the band contour produced by broadening out these rotational lines until they merge (which may be done experimentally by adding rare gas). The middle panel shows the quantum band contour (solid line) compared with the correspondence principle classical contour (open circles) calculated in the limit of quantum mechanics as Planck's constant $h \to 0$. Two simple and relatively small quantum corrections have been applied to the correspondence principle classical band contour. The rotational correction accounts for the different population ratios in classical and quantum mechanics of the rotational states connected by the transition. The vibrational correction is a frequency shift due to the fact that the classical diatomic vibrates at $\sim kT$ (~ 200 cm^{-1}), near the bottom of the well and thus in a largely harmonic region, while the quantum diatomic is sampling the potential in the $\sim \hbar\omega_o$ (~ 2000 cm^{-1}) energy range in which the effects of anharmonicity are more pronounced. As can be seen, after these quantum corrections the correspondence principle classical and the quantum band contours agree almost exactly, demonstrating that the band contour can be understood classically. The lower panel shows again the quantum band contour (solid line) and superimposed on it the quantum corrected Newtonian classical band contour (triangles) from classical molecular dynamics, classical linear response theory and classical statistical mechanical ensemble averaging. The filled circles show the shape of the experimental band contour for CO with added He as measured by ARMSTRONG and WELSH [9].

We see that the band contour results for all four of the following agree: i) quantum time-dependent perturbation theory, ii) quantum-corrected correspondence principle classical mechanics, iii) quantum-corrected Newtonian classical mechanics, and iv) experimental measurement. Thus, the vibrational-rotational band contour can be understood on the basis of classical trajectories of the atoms.

If we mix CO in Ar and keep increasing the Ar pressure, both by Newtonian classical mechanics [6] and by experimental measurement [10] the P and R branch peaks increasingly meld into one another until they fuse into the usual single-peaked liquid state vibrational band contour [11]. Therefore, in the liquid state as well, one can compute and understand the vibrational band contour in terms of classical atomic trajectories.

Finally, the techniques described here can be extended to treat the non-equilibrium domain, so that one can compute transient ir and Raman spectra during the course of picosecond processes, for example chemical reactions in solution. In this way, one can hope to combine the computation and the measurement of picosecond transient vibrational spectra to discover the microscopic mechanism, the atomic trajectories during chemical reactions in solution.

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